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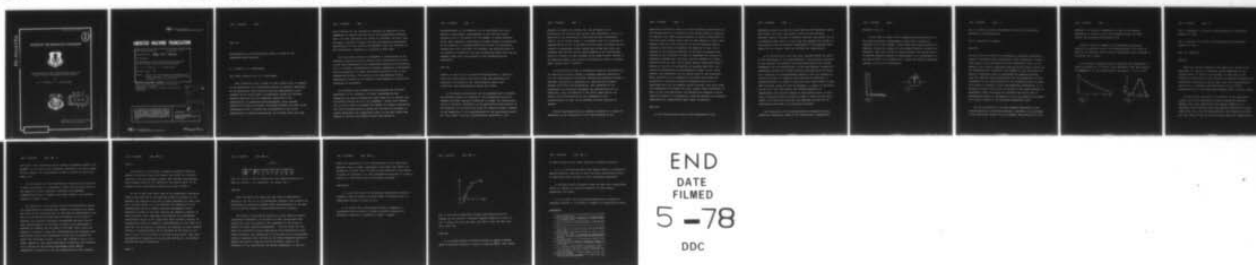
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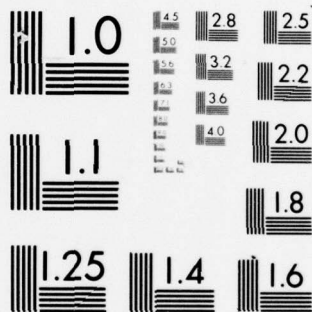
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THE MECHANISM OF THE CRYSTALLIZING ACTION OF
SOLIDS ON THE SUPERCOOLED WATER AEROSOLS

by

M. V. Tovbin, G. G. Buderaskaya



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THE MECHANISM OF THE CRYSTALLIZING ACTION OF SOLIDS ON THE
SUPERCOOLED WATER AEROSOLS.

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Many researchers over a number of years conduct work on research on the mechanism of the crystallizing action of different substances on the supercooled water aerosols. With the investigation of new reagents for an active effect on supercooled clouds and mist/fogs decisive importance has the laboratory evaluation of the effectiveness of synthesized specimen/samples, which precedes laborious and bulky field tests. One should consider also that by the contemporary state of problem the investigation of new active preparations is conducted empirically. As is known, until this time

sole criterion for the preliminary selection of substances is the resemblance of crystal lattices of ice and crystallizing substance which, as shows experiment, not always is justified, and main, does not make it possible to obtain even the approximately quantitative characteristic of the activity of substance. Thus, the selection of the crystallizing substances is conducted by mass tests.

The ice-forming activity of substance is characterized by the threshold temperature and the outcrop of the crystallization nuclei at the given temperature of the supercooled mist/fog from calculation on 1 g of reagent. Experimentally threshold temperature is determined from the appearance of single crystalline particles of ice in the supercooled mist/fog. The outcrop of the crystallization nuclei significantly depends on the method of the dispersion of reagent and conditions of experiment.

Are suggested many procedures for determining the threshold temperature of ice formation. In Soviet investigations most frequently use cooling chambers of large volume [6]. In earlier work was applied cooling box [11, 13], sometimes - Wilson cloud chamber [4]. In recent years is proposed the chamber of original construction with strict thermostating in volume [3], and also the procedure of cooling shaft/mine with temperature lapse [2]. The most widely used methods of applying the chambers during mass testing of

specimen/samples are inconvenient due to unwieldiness and labor expense of experiments. Inconvenience is also that the tested substance must be introduced into the chamber in highly dispersed state. Under laboratory conditions are always feasible the operations of the conversion of specimen/sample into aerosol by sublimation, fragmentation with explosion, etc. Finally, the application/use of the chambers is impeded by the need to thoroughly clean them from the reagents, which were being applied in the preceding/previous experiments.

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However, in spite of the indicated deficiency/lacks, it should be noted that these methods give thus far the only possibility of estimating the outcrop of the crystallization nuclei under conditions, which approximately imitate real cloud.

In the present investigation was the expressed goal to develop the convenient method of research on the crystallizing action of reagents and under identical conditions to compare the crystallizing action of different substances. As the quantitative characteristic of the intensity of this action can serve the caused by reagent increase in the temperature of the crystallization of the supercooled aerosol $\Delta T = T - T_0$ (where T and T_0) crystallization temperature in the

presence of reagent and without it). The procedure of the determination of value ΔT must satisfy some requirements. First, it must provide the possibility of obtaining the well reproducible results. In the second place, it is necessary that the conditions of experimentation as far as possible would be close to thereby that are created in supercooled clouds. Taking into account that which was presented were carried out the investigations of the crystallizing action of reagents on model systems. As the model of water aerosol in the developed method, was utilized the emulsion of water in slightly polar viscous fluid - vaseline.

In the literature there is information about the observation of ice formation by optical method in opposite emulsions (water/oil) [7]. For investigations the authors obtained the emulsion of water in vaseline, stabilized by emulsifier T-2 (esterification product maximum fatty acids and polyglycerol). For conducting of our experiments, we considered impossible the application/use of an emulsifier, since the addition of the latter could distort the picture of the determination of the temperature of the crystallization of water in the emulsion with the additions of reagent.

She was experimentally by us studied the effect of a series of substances on the temperature of the crystallization of the

supercooled emulsion of water in oil not containing stabilizers. For the target/purpose of an increase in the kinetic emulsion stability to vaseline, they added certain quantity of carbon tetrachloride so that the forming mixture would have the same density as water. This mixture, named oil, was utilized by us as the dispersive medium during the production of emulsion. The emulsion of water in oil obtained by two different methods. In the first the emulsion was obtained by the dispersion of water in instrument for grinding of biological preparations. For this, into the container of crusher, filled 50 ml of oil and 1 ml of water. Mixture they mixed during 5 minutes at the rate of the rotation of agitator 6000 r/min. As a result was obtained the uniform emulsion of water in oil, which, however, was understable and for several hours it was stratified. This, apparently, it is explained to the facts that during the preparation of emulsion by means of energetic mixing into it unavoidably fall the air bubbles, which, floating, they carry along with themselves the droplets of water, causing their coalescence. In spite of this deficiency/lack, the obtained thus emulsion of water could be utilized for investigation, since the duration of conducting experiments was comparatively small (about 30 minutes).

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In the second method, based on the condensation of the

superheated steam in cooled oil, were obtained the emulsions, kinetic more stable. For this, into cooled to 0°C oil from fine/thin capillary during 15 seconds at constant velocity, they passed the jet of overheated water vapor. In this case, was obtained very stable in time emulsion with the constant condensation of the dispersed phase (about 20/o by volume), which was utilized for investigation.

It is interesting to note that data, obtained during the study of the temperature of the crystallization of the emulsions, prepared by the described two methods, will agree sufficiently well between themselves. For the characteristic of the used emulsion, prepared by condensation method, was studied particle distribution of the water in it according to size/dimensions. Figures 1 gives the spectrum of the drops of water in emulsion. Along the axis of ordinates, is deposit/postponed the number of particles (o/o) whose radius is less than the datum, along the axis of abscissas - a radius of particles r μm . As can be seen from figure, the studied emulsions are polydisperse, with distinct maximum in distribution curve. In this case, a greatest quantity of drops of water in emulsion they have a radius 6 μm . These data show that this emulsion can serve as the sufficiently good model of natural water aerosols.

The temperature of the crystallization of emulsions she was studied by thermograph method at the installation, schematically

depicted on Fig. 2.

In test tube A, filled 10ml of emulsion and was placed into it the copper-constantan thermocouple B. Test tube A on plug was inserted into cooling chamber C whose walls were thermo-insulated by asbestos, through the chamber at the constant velocity, recorded by rheometer, they blow, cooled by liquid nitrogen, and through each of 30 seconds recorded readings of thermocouple B on a galvanometer of the type M-198/3. As an example Fig. 3 gives the typical thermogram, obtained in one of the experiments.

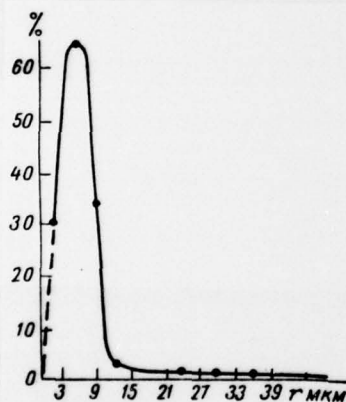


Fig. 1

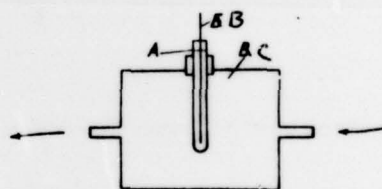


Fig. 2

Fig. 1. Curved of particle distribution of water in the emulsion according to size/dimensions.

Fig. 2. Installation diagram.

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As can be seen from figure, on thermogram is distinctly observable a series of exothermic peaks (temperature, which corresponds to each of these peaks, it was determined from the calibration curve), of the caused by the freezing individual fractions of the drops of water, by the accompanied heat liberation. The presence on the thermogram of a series of exothermic peaks is represented by completely natural, since the emulsions being investigated were poly-dispersed, and the temperature of the crystallization of the supercooled drops of water, as is known, it depends on their size/dimension. Furthermore, it is necessary to keep in mind that the process of the crystallization of supercooled liquid fluctuates and therefore even in the case of monodisperse systems on thermogram it was to be expected the presence of a series of peaks in the determined temperature range.

For the calculation of the most probable temperature of the crystallization of polydisperse emulsion, obviously, it is necessary to use statistical method. For this purpose, they placed not to the

exchange of 10 parallel experiments (so that on the obtained thermograms it would be, about 100 exothermic peaks) and their results were processed statistically [4].

Figures 4 gives an example of the histogram, constructed according to empirical data of the freezing points of the drops of water in the emulsion, and the evened distribution curve according to the normal law of Gauss.

In this case probability that the empirical law corresponds to normal distribution, is 99.70/o. with reliability 0.95, most probable the temperature of the crystallization of drops $\bar{T} = -17.3 \pm 0.5^\circ\text{C}$.

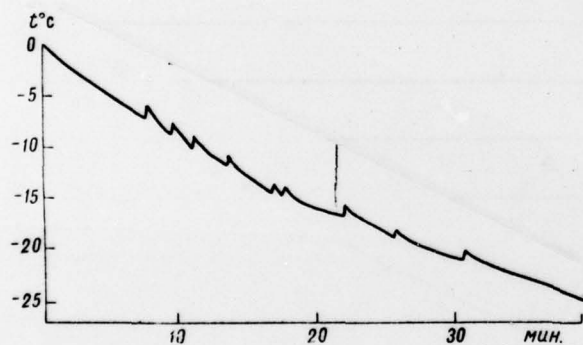


Fig. 3

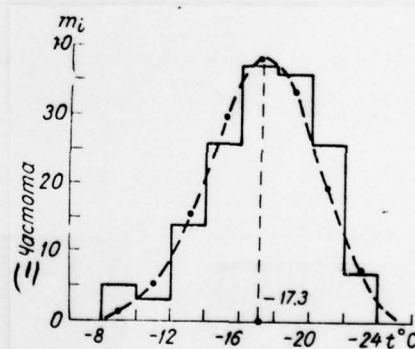


Fig. 4

Fig. 3. Thermogram of process of crystallization of supercooled emulsion of water.

Fig. 4. Histogram of process of crystallization of supercooled emulsion of water.

Key: (1). Frequency.

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Then was initiated research on the effect of a series of the substances of a series of substances on the temperature of the crystallization of water in the emulsion. In this case, as the subjects of investigation, were selected the reagents, possessing the considerable crystallizing action (AgJ, PbJ₂, CuS, phloroglucinol), and also for a comparison some substances, the not calling crystallizations of the supercooled aerosols (AgCl, CdS, PbS, CaCO₃).

As can be seen from Table 1, the results of the experiments, carried out with the emulsions of water, obtained by different methods, will agree sufficiently well between themselves. In accordance with literature data, the greatest crystallizing action, possess AgJ, PbJ₂, CuS and phloroglucinol. Such substances as AgCl, CdS, PbS, CaCO₃, either do not in practice affect the temperature of

the crystallization of water or even several it they decrease (CaCO_3).

Given data also show that the proposed method can be used to evaluate and comparison of the crystallizing action of different substances on the supercooled water aerosols.

By the very interesting to us is represented the established/installed experimentally fact of a sharp reduction in the emulsion stability of water in oil in the presence of a series of the crystallizing reagents. This fact proved to be somewhat not expected. As is known, highly dispersed powders can be the stabilizers of emulsions. In this case, hydrophobic powders (for example, carbon black) will stabilize opposite emulsions (of type "water-in-oil"). As is known, the cases of a reduction in the emulsion stability in the presence of highly dispersed powders, until now, are not described. The stabilization of emulsions by powders, and also the reverse process of a reduction in the emulsion stability, undoubtedly represent the surface phenomena, connected with the accumulation of reagents on the boundary of two nonmiscible liquids.

Table 1.

(1) Вещество	(2) Эмульсия, полученная дисперсионным методом		(3) Эмульсия, полученная конденсационным методом	
	T	ΔT	T	ΔT
Вода (4)	-17,3	—	-14	—
AgJ (5)	-8,5	8,8	-5,8	8,2
Флороглюцин	—	—	-6,8	7,2
PbJ ₂	-9,6	7,7	-6,9	7,1
HgJ	—	—	-8,9	5,1
CuS	—	—	-9,3	4,7
CdS	—	—	-12,5	1,5
AgCl	—	—	-12,7	1,3
PbS	—	—	-14,4	-0,4
CaCO ₃	-20	-2,7	-15,7	-1,7

Key: (1). Substance. (2). Emulsion, obtained by dispersion method.
 (3). Emulsion, obtained by condensation method. (4). Water. (5)
 Phloroglucinol.

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In connection with this it is very interesting to compare the
 action of reagents with the character of its adsorptive interaction

with water. This interaction can be studied by different methods, for example, by the study of the adsorption isotherms of the water vapors on this reagent, the determination of heat of wetting of solid with water, etc.

On the character of the interaction of the area of the particle of solid with water, it is possible to judge also by their effect on the stability of water emulsions. Therefore was comparably crystallizing action of reagents with their effect on the emulsion stability of water in oil.

For research on this question, was utilized Reh binder's method [8]. Experimentation technique was reduced to following. The beaker was filled by the distilled water at the level of approximately 5 cm, and to it was filled the same layer of vaseline. In the layer of vaseline from fine/thin capillary, was extruded the small drop of water (size/dimension of the drops of water in all experiments it remained the constant and was equal to 0.05 ml), which slowly was omitted to interface a water-oil. Experimentally was determined time after which occurred the coalescence of drop with the surface of water (the "lifetime" of drop - τ s.). The lifetime of drop, as is known, depends on many random experimental conditions, and therefore it is carried out 100 parallel measurements which undergo mathematical treatment [1], for the determination of most probable

value r .

For research on the effect of solids on emulsion stability instead of the water layer into beaker, was filled the colloidal solution of the corresponding reagent. The obtained experimentally most probable values of the lifetime of the drop of water in the presence of the investigated reagents are given in Table 2.

As can be seen from table, some of the investigated substances cause a sharp decrease in the emulsion stability of water in oil, moreover the lifetime of the drop of water decreases 3-4 times. This fact, as noted above, it is not expected. The mechanism of this destabilizing action of powders requires supplementary study. Attention is drawn to that that decrease the emulsion stability of water precisely those substances which possess the considerable crystallizing action on the supercooled water aerosols. Between the crystallizing effect of reagents, characterizable by that found by us value ΔT , and its ability to decrease the stability of water emulsion (which it is quantitatively can be evaluated by the value of r_0/r where r_0 and r are a lifetime of the drop of pure water, also, with the addition of reagents), as can be seen from Fig. 5, is observed sufficiently clear correlation.

Table 2.

Table 2

(1)
Влияние твердых веществ на устойчивость эмульсии воды в вазелиновом масле

Вещество . . .	Вода (2)	AgJ	PbJ ₂	HgJ	CuS	AgCl	CaS	PbS	CaCO ₃
τ сек. (3)	131	27	45	57	75	99	99	128	176

Key: (1). Effect of solid substances on the emulsion stability of water in vaseline. (2). Substance. (3). Water. (4). s.

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This conclusion will agree with the views of researchers's series [9, 12, 15]. It is of considerable interest, since surface can be modified by adsorptive methods, which open/discloses the new ways of an artificial change of crystallizing action of reagents.

For testing of last/latter position, we were conducted several preliminary experiments. In the first of them, was hydrophilized surface AgJ. This was reached by the adsorption of the traces of gelatin by highly dispersed suspensions AgJ. It turned out that after this adsorptive surface modification the crystallizing action sharply descends. The possibility of an increase in the crystallizing action of substances was verified on the highly dispersed powders of quartz. The quartz, which has crystal structure, close to the structure of ice, nevertheless, as showed experiments, it does not

affect the temperature of the crystallization of the supercooled emulsion. This is caused, apparently by the facts that quartz has hydrophilic surface. After the partial waterproofing of the surface of quartz by treatment of it with dimethyldichlorosilane it became to exhibit the sufficiently high crystallizing activity.

Conclusions.

1. Is described method of determining crystallizing action of reagents, based on research on their effect on freezing point of supercooled emulsion of water in oil.

2. Is assumed that crystallizing action of reagents on supercooled water aerosols is caused by specific character of adsorptive processes on interface of water - reagent.

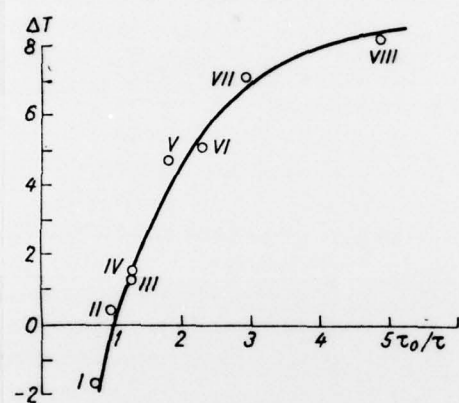


Fig. 5. Correlation dependence between crystallizing action of reagent and its ability to decrease emulsion stability of water in oil. I) CaCO_3 , II) PbS , III) AgCl , IV) CdS , V) CuS , VI) HgS , VII) PbJ_2 , VIII) AgJ .

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3. Is studied effect of series of solids in highly dispersed state on emulsion stability of water in vaseline. ⁵ Shown, that series

of solid reagents causes sharp decrease in emulsion stability.

4. It is established/installed that between ability of reagents to decrease emulsion stability of water and their crystallizing action on supercooled water aerosols is clear correlation dependence.

5. Findings confirm assumption about the fact that crystallizing action of reagents is caused by character of their surface interaction with water.

6. It is shown, that by surface modification of reagent by adsorptive methods it is possible to affect its crystallizing action.

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